Calculating the Density and Viscosity of Multi-Component Gas Mixtures

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The goal of the present work is to find a simple way to calculate the density and viscosity of the mixtures composed of N2, O2, CO2, Ar, and H2O that will be used in the Exhaust Meter Calibration Facility (EMCF). Density will be used to convert the mass flow rates measured by critical nozzles to the volumetric flow rate which is often the output of the meter under test. Viscosity is needed to calculate the Reynolds number of the flow, as it will often be the independent variable for the presentation of calibration data for the meter under test. Other quantities such as thermal conductivity and specific heat may also be required for calculating the appropriate dimensionless quantities for presentation of calibration data from thermal meters, but the methods for their calculation has not been undertaken as yet.

The methods of calculation will be programmed in a data acquisition and control program and should involve simple mathematics to minimize programming mistakes, programming costs, execution times, and storage space. Yet to not impact the uncertainty analysis significantly, the method should yield values within 0.1% for density. For viscosity, values within 4% are acceptable since experimental viscosity measurements are not very accurate: deviations between the most sophisticated calculation methods and experimental results are often greater than 2%, and calibration factors are not strong functions of the Reynolds number. The range of temperatures to be used is from 270 K to 700 K, and the pressure is essentially atmospheric pressure (101325 Pa).

Before outlining the simplified equations for calculating the density and viscosity

Density from the Virial Equation

The equation for the density of an ideal gas is:

$$\rho_{ideal} := \frac{P \cdot M}{R \cdot T \cdot 100^3} \qquad (1)$$

where ρ is in $\frac{g}{cm^3}$, P is pressure in Pa, M is the molecular weight, R is the universal gas constant 8.31451 $\frac{J}{mol \cdot K}$, and T is the temperature in K. To correct for the non-ideal behavior of a gas, the *compressibility factor*, Z, may be introduced to create a virial equation of state:

$$\rho := \frac{P \cdot M}{R \cdot T \cdot 100^3 \cdot Z}^{\blacksquare} \tag{2}$$

$$Z := 1 + B \cdot \rho + C \cdot \rho^2 + D \cdot \rho^{3\blacksquare} \tag{3}$$

where B, C, and D are the second, third, and fourth *virial coefficients*. Their values may be found experimentally over a range of pressures and temperatures, or they may be calculated by the approaches of statistical mechanics and intermolecular potential energy functions. From the molecular theory point of view, B accounts for the interations of pairs of molecules, C accounts for interactions of sets of three molecules, etcetera. At high temperatures and low pressures, molecules behave more like point masses, and gas behavior approaches the ideal gas law (Z approaches 1). Analysis of values of C and D for the gases of interest over the temperatures and pressures of interest, shows that the third (and higher) virial coefficients are negligible. In the virial equation, ρ_{ideal} can be used instead of the real gas density without significant increase in error, thereby avoiding the need for an iterative solution for ρ. Hence, the problem of calculating density now centers on calculating the second virial coefficient, B. As explained in the following section, the second virial coefficient is related to the potential energy between pairs of molecules and the theory of intermolecular forces can be used to predict the dependence of B on temperature.
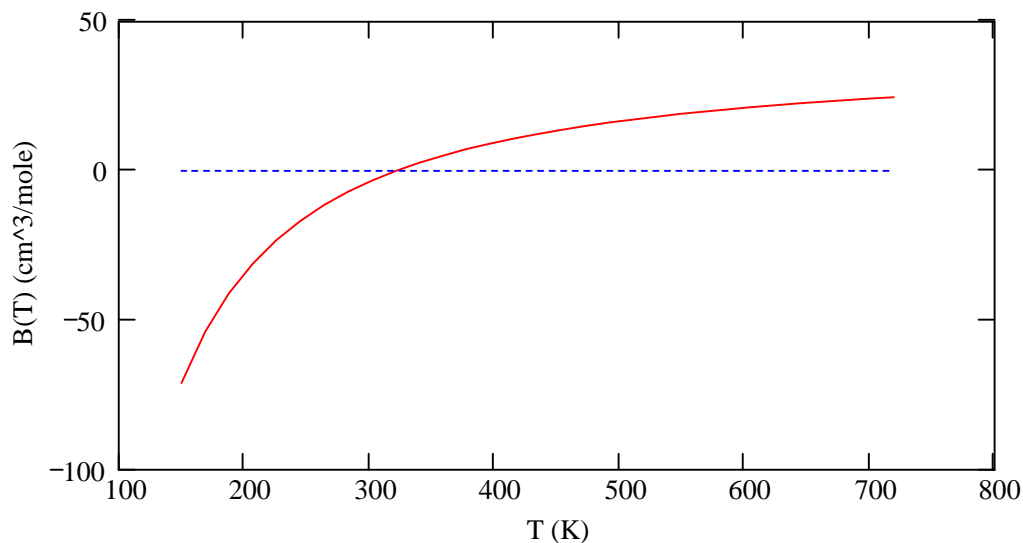

Figure 1: The second virial coefficient for N2-N2 interactions versus temperature. At higher temperatures, approaches zero and the gas approaches ideal gas law behavior.

The Principle of Corresponding States

The forces between molecules and many of the bulk properties of a gas are governed by the intermolecular potential energy function, U. The potential energy function leads to an attractive force between molecule pairs at long range, and strong repulsive forces at short range. Numerous potential energy functions have been proposed and most of them have the intermolecular forces characterized by two parameters: the separation for zero potential energy, σ, and the minimum potential energy (or well depth), ε. A commonly used function is the Lennard-Jones potential:

$$U(r) := 4 \cdot \varepsilon \cdot \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]^{\blacksquare} \qquad\qquad (4)$$

where r is the intermolecular separation.
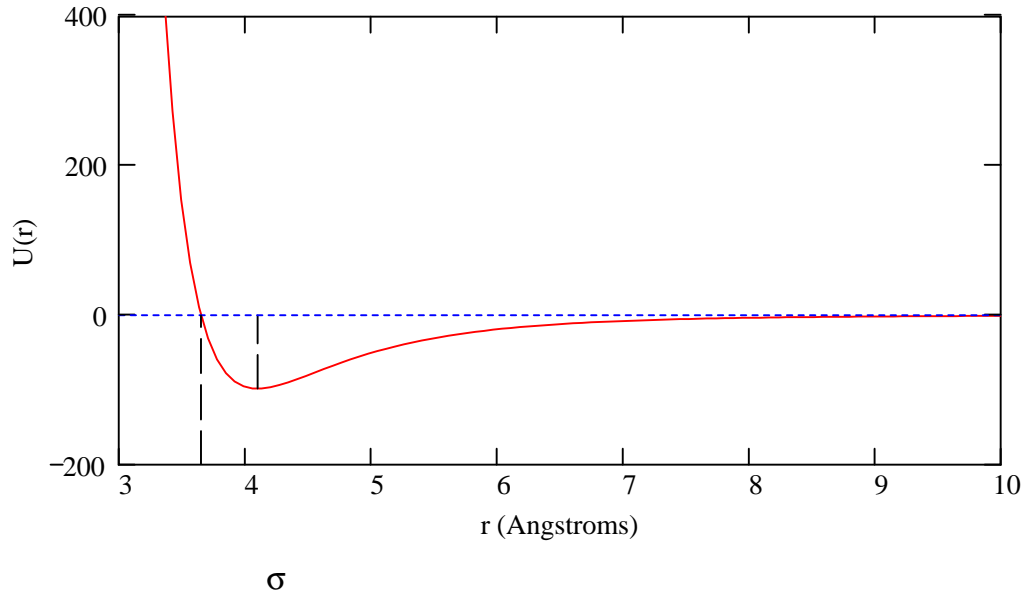

Figure 2: The Lennard-Jones intermolecular potential energy function for N2 labeled with the two characterizing parameters, σ and ε.

The second virial coefficient and viscosity can be calculated via certain integrals if the potential function is known. But since the potential function cannot be predicted exactly, what is actually done is: experiments are performed on a gas to measure the second virial coefficient or viscosity over a range of temperatures, the data are best fitted to arrive at values of σ and ε for that gas, these values are used to calculate B and viscosity under other conditions.

Potential functions which are of the form $U(r) := \varepsilon \cdot F \left(\frac{r}{\sigma} \right)^{\blacksquare}$ (as the

Lennard-Jones

Lennard-Jones

potential is) have the useful characteristic that their integrals can be written in terms of a single variable, the reduced temperature, $T_r := \dfrac{k \cdot T}{\varepsilon}$, where k is the Boltzmann

constant $= 1.380658 \cdot 10^{-23} \dfrac{J}{K}$. With this approach, the second virial coefficient can be written as:

$$B(T) := b_0 \cdot B_r(T_r) \qquad\qquad\qquad (5)$$

where b_0 is a gas dependent constant and B_r is a *reduced second virial coefficient* which can be used for many different gases that obey the same potential function. A similar quantity, $\Omega_r(2,2)$, the *reduced collision integral*, can be used to calculate viscosity, η, by the following equation:

$$\eta := \frac{5}{16} \cdot \left(\frac{m \cdot k \cdot T}{\pi} \right)^{\frac{1}{2}} \cdot \frac{1}{\sigma^2 \cdot \Omega_r(2,2)} \qquad\qquad (6)$$

where m is the mass of a molecule, $\dfrac{M}{N_A}$, and N_A is Avagadro's number $=$ $6.0221367 \cdot 10^{23} \ mol^{-1}$.

While the Lennard-Jones potential applies well to noble gases and to approximately spherical polyatomic molecules, it does not model the behavior of polar molecules such as water. Polar molecules are more compressible than non-polar molecules due to additional electrical attractions. Thus for polar molecules the Stockmayer potential function has been introduced which includes a third parameter,

and the dipole moment parameter, δ_{max}.

Proposed Methods of Calculation

Thorough treatments of the most sophisticated methods for calculating the second virial coefficient and viscosity of multi-component gas mixtures can be found in Bzowski *et al.*, Maitland *et al.*, and Hirshfelder *et al.* The following portion of this document will be devoted to explaining a simplified approach designed to meet the requirements outlined in the introduction.

Density Calculations

The second virial coefficient for a gas mixture, B_{mix}, is normally calculated by the following equation:

$$B_{mix} := \sum_i \sum_j B_{i,j} \cdot x_i \cdot x_j \qquad \blacksquare \qquad (7)$$

which for a three component gas mixture can be written as:

$$B_{mix} := (x_1)^2 \cdot B_{1,1} + 2 \cdot x_1 \cdot x_2 \cdot B_{1,2} + (x_2)^2 \cdot B_{2,2} \qquad \blacksquare \qquad (8)$$

where x_i and x_j are the mole fraction of the ith and jth gas components, and $B_{i,j}$ is the virial coefficient due to the molecular interactions of components i and j. Hence, if $i = j$, $B_{i,j}$ represents the pure gas virial coefficient, that due to interaction of molecules of the same species (a *self-interaction* virial coefficient). But if $i \neq j$, $B_{i,j}$ represents interactions between different species (a *cross-interaction* virial coefficient). Elaborate methods are available for predicting cross virial coefficients (see Bzowski *et al.*). The proposed simplified method uses polynomial equations fitted to experimental virial coefficient data to predict the values of $B_{i,j}$. Further, only the terms of summation (7) that are significant for calculation of B_{mix} were included.

To determine which terms of summation (7) were significant, values of $B_{i,j}$ were found (Dymond and Smith) for the worst case conditions ($T := 270$ K) and B_{mix}

	x_{N2}	x_{O2}	x_{CO2}	x_{Ar}	x_{H2O}
Maximum CO2	0.7364	0.1374	0.0060	0.0085	0.1117
Maximum O2	0.7769	0.2035	0.0008	0.0090	0.0098
Half O2 consumed	0.7910	0.1000	0.0650	0.0090	0.0350
Dry air	0.7810	0.2095	0.0003	0.0092	0.0000
Saturated air at 300 K	0.7543	0.2023	0.0003	0.0089	0.0342
Saturated air at 320 K	0.6992	0.1875	0.0003	0.0082	0.1048
Saturated air at 327 K	0.6646	0.1783	0.0002	0.0078	0.1491

Table 1: Test case gas mixture compositions set up to determine significant contributions to B_{mix}

Any summation term which when removed caused density changes less than 0.01% for all of the test cases, was considered negligible. The significant $B_{i,j}$'s were found to be: N2-N2, N2-O2, N2-CO2, N2-H2O, O2-H2O, CO2-CO2, CO2-H2O, and H2O-H2O.

Dymond and Smith have compiled a very complete set of values for the self- and cross-interaction virial coefficients from the available literature. Kehiaian presents polynomial equation best fit coefficients for predicting B for the self-interaction virial coefficients for the gases of interest here. However, he gives no coefficients for cross-interation B's, so it was necessary to perform best fits of the form suggested by Kehiaian on data found in Dymond and Smith. For some gas pairs, there was little or no experimental $B_{i,j}$ data available (for example O2-H2O), and in these cases the method of corresponding states as demonstrated by Hirschfelder *et al.*, p. 223 was utilized to generate more points for the polynomial fitting. The form of the polynomial fit and the best fit coefficients are given below:

$$B_{i,j} := \sum_{k=0}^{n} A_k \cdot \left(\frac{298.15}{T} - 1 \right)^k \qquad (9)$$

	N2-N2	N2-O2	N2-CO2	N2-H2O	O2-H2O	CO2-CO2	CO2-H2O	H2O-H2O
A0	-4	-10.2	-39.8	-41.2	-59.2	-127	-138.2	-1158
A1	-56	-59.4	-108.3	-104.1	-108.5	-288	-221.5	-5157
A2	-12	-9.93	-46.2	-79.4	-23.2	-118	22	-10301
A3								-10597
A4								-4415

Table 2: Best fit coefficients for calculating the second virial coefficients for the eight significant gas interactions.

The $B_{i,j}$'s calculated by equation (9) and Table 2 are used in the summation of equation (7) (with the negligible terms dropped) to determine B_{mix}. Also needed to calculate the mixture density is the mole-fraction-weighted molecular weight of the mixture:

$$M_{mix} := \sum_{i} M_i \cdot x_i \qquad (10)$$

(In calculating the molecular weight of the mixture, all components are considered significant.) Finally the density of the mixture is calculated by combining equations (1), (2), and (3), and using the "mixture" quantities:

$$\rho_{mix} := \frac{P \cdot M_{mix}}{R \cdot 100^3 \cdot T \cdot \left(1 + B_{mix} \cdot \dfrac{P}{R \cdot T \cdot 100^3}\right)} \qquad \blacksquare \qquad (11)$$

This equation yields density in $\dfrac{g}{cm^3}$ when P is in Pa, R has units $\dfrac{J}{mol \cdot K}$, and T is in degrees K.

Viscosity Calculations

The principle of corresponding states was applied to calculate the viscosity of the pure gas components of the mixture. The pure gas viscosities were used to calculate the mixture viscosity by the method of Herning and Zipperer.

In using the principle of corresponding states, the values of $\dfrac{\varepsilon}{k}$, σ, and molecular
weight were as shown below:

	$\dfrac{\varepsilon}{k}$ (K)	σ (A)	M
N2	98.4	3.652	28.0135
O2	121.1	3.407	31.9988
CO2	245.3	3.769	44.0098
Ar	141.5	3.35	39.948
H2O	775	2.5	18.0153

Table 3: Molecular constants used in corresponding states calculations.

The values of $\dfrac{\varepsilon}{k}$ and σ for the non-polar molecules were taken from Bzowski *et al.,* the values for water (not covered by Bzowski *et al.*) were obtained from Monchick and Mason. The reduced temperature is calculated by dividing the temperature in degrees K by $\dfrac{\varepsilon}{k}$. The reduced collision integral for the nonploar gases is calculated by a best fit formula:

$$\Omega_r(2,2) := \exp\left(\begin{array}{l} 0.46649 - 0.57015 \cdot \ln(T_r) + 0.19164 \cdot \ln(T_r)^2 \ ... \\ + -0.03708 \cdot \ln(T_r)^3 + 0.00241 \cdot \ln(T_r)^4 \end{array}\right)^{\blacksquare} \qquad (12)$$

which is from Maitland *et al.* (Appendix 3). For the polar molecule, water, a fit has been performed on tabular data presented in Monchick and Mason (p. 1685) for the Stockmayer potential with the dipole moment parameter, $\delta_{max} := 1.0$ for water.

$$\Omega_{rH2O}(2,2) := \exp\left(0.59983 - 0.52318 \cdot \ln(T_r) + 0.07175 \cdot \ln(T_r)^2\right)^{\blacksquare} \qquad (13)$$

The viscosity for the pure components of the mixture can be calculated using equation (6), which with the values of constants and conversion factors combined becomes:

$$\eta := \frac{5}{16} \cdot \frac{\left(M \cdot 7.298 \cdot 10^{-41} \cdot T\right)^{\frac{1}{2}^{\blacksquare}}}{\left(\sigma \cdot 10^{-8}\right)^2 \cdot \Omega_r(2,2)} \qquad (14)$$

with σ in Angstroms, T in degrees K, M the molecular weight, and $\Omega_r(2,2)$ the result from equations (12) or (13). To calculate the viscosity of a multi-component gas mixture, the method of Herning and Zipperer was selected, which uses the equation:

$$\eta_{mix} := \sum_i \frac{x_i \cdot \eta_i}{\sum_j x_j \cdot \left(\frac{M_j}{M_i}\right)^{\frac{1}{2}}}^{\blacksquare} \qquad (15)$$

This method was selected based on its simplicity and on testing which shows that it generally gives results that are correct within 2% (Herning and Zipperer, Touloukian *et al.*).

Verification of Accuracy

To confirm that the calculation methods are acceptably accurate in the range of

Pure Gases

Reference values of density and viscosity for pure N2, O2, CO2, Ar, and H2O

percent error of the calculated density and viscosity over a range of temperatures (all at 101325 Pa pressure).

T (K)	Reference Density (g/cm^3)	Calculated Density (g/cm^3)	%	Reference Viscosity (g/s/cm)	Calculated Viscosity (g/s/cm)	%
300	1.1383E-3	1.1381E-3	-0.016%	1.7900E-4	1.7961E-4	0.341%
400	8.5331E-4	8.5320E-4	-0.013%	2.2200E-4	2.2256E-4	0.252%
500	6.8256E-4	6.8250E-4	-0.009%	2.6100E-4	2.6086E-4	-0.054%
600	5.6878E-4	5.6873E-4	-0.009%	2.9600E-4	2.9591E-4	-0.030%

Table 4: Accuracy of calculated density and viscosity values for Nitrogen.

T (K)	Reference Density (g/cm^3)	Calculated Density (g/cm^3)	%	Reference Viscosity (g/s/cm)	Calculated Viscosity (g/s/cm)	%
300	1.3007E-3	1.2998E-3	-0.069%	2.0800E-4	2.0782E-4	-0.087%
400	9.7494E-4	9.7489E-4	-0.005%	2.6100E-4	2.6007E-4	-0.356%
500	7.7978E-4	7.7991E-4	0.017%	3.0800E-4	3.0663E-4	-0.445%
600	6.4977E-4	6.4992E-4	0.023%	3.5100E-4	3.4914E-4	-0.530%

Table 5: Accuracy of calculated density and viscosity values for Oxygen.

T (K)	Reference Density (g/cm^3)	Calculated Density (g/cm^3)	%	Reference Viscosity (g/s/cm)	Calculated Viscosity (g/s/cm)	%
300	1.7967E-3	1.7969E-3	0.011%	1.5000E-4	1.5078E-4	0.520%
400	1.3432E-3	1.3433E-3	0.007%	1.9700E-4	1.9825E-4	0.635%
500	1.0733E-3	1.0734E-3	0.009%	2.4000E-4	2.4118E-4	0.492%
600	8.9414E-4	8.9410E-4	-0.004%	2.8000E-4	2.8054E-4	0.193%

Table 6: Accuracy of calculated density and viscosity values for Carbon Dioxide.

T (K)	Reference Density (g/cm^3)	Calculated Density (g/cm^3)	%	Reference Viscosity (g/s/cm)	Calculated Viscosity (g/s/cm)	%
300	1.6236E-3	1.6228E-3	-0.049%	2.2900E-4	2.2838E-4	-0.271%
400	1.2170E-3	1.2171E-3	0.009%	2.8800E-4	2.8829E-4	0.101%
500	9.7340E-4	9.7365E-4	0.026%	3.4200E-4	3.4173E-4	-0.079%
600	8.1110E-4	8.1138E-4	0.035%	3.9000E-4	3.9048E-4	0.123%

Table 7: Accuracy of calculated density and viscosity values for Argon.

T (K)	Reference Density (g/cm^3)	Calculated Density (g/cm^3)	%	Reference Viscosity (g/s/cm)	Calculated Viscosity (g/s/cm)	%
300	-	7.6691E-4	-	1.0000E-4	9.8342E-5	-1.658%
400	5.5493E-4	5.5488E-4	-0.009%	1.3300E-4	1.3646E-4	2.602%
500	4.4095E-4	4.4097E-4	0.005%	1.7300E-4	1.7451E-4	0.873%
600	3.6670E-4	3.6668E-4	-0.005%	2.1400E-4	2.1221E-4	-0.836%

Table 8: Accuracy of calculated density and viscosity values for Water.

For the pure gas test cases, the greatest error in the density values occurred for O2 at 300 K, where the error was 0.069%. Water posed the greatest difficulties for the viscosity calculations, with an error of 2.6% at 400 K. However, the uncertainty in the reference viscosity data is more than half the magnitude of the difference between the calculated and reference values (Sengers and Watson). Therefore, the errors in the values from the simplified density and viscosity calculations were deemed acceptable.

Multi-Component Gas Mixtures

Test case gas mixture compositions were postulated and comparisons made between the values calculated by the simplified equations described in the previous section and the best available reference data. For reference data, twelve test case compositions with experimentally measured viscosity data were compiled by Golubev. Also, five of the seven mixture compositions listed in Table 1 were examined at 700 K and nominally 300 K. Experimental density values could be obtained for two of these fourteen cases from data in the *ASHRAE Handbook*. Also available was the program Supertrapp, written by Ely and Huber, which uses the method of extended corresponding states to compute the properties of mixtures. While primarily designed to work for hydrocarbon mixtures with small amounts of other components, it was found to achieve good agreement with available test case experimental data, and hence was used to generate reference data values that were otherwise unavailable.

Tables 9 and 10 present the results of the comparison of reference and calculated values for the gas mixture test cases. The column labeled "%" is the percent difference between the calculated values and the best available reference data (sometimes experimental, sometimes Supertrapp). For density, the largest error was 0.04% for the "Half consumed O2" case at 300 K. For viscosity, the largest errors of about 4.5% were found at the high temperature conditions, slightly above the accuracy goal for viscosity of 4%.

Conclusions

The simplified calculations for obtaining the density and viscosity of gas mixtures generated by the EMCF were found to be an acceptable balance between ease of implementation and accuracy of results. The accuracy of the calculated density is about twice as good as the 0.1% goal, while calculated viscosity is about 0.5% worse than the 4% goal. The worst errors in viscosity are under the high temperature conditions. The method of corresponding states used to calculate viscosity could be readily used to give the thermal conductivity of gas mixtures as well. Further study seeking simple algorithms that calculate the properties of multi-component gas mixtures and testing of those algorithms would be useful.

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